

## MARS REGOLITH VERSUS SNC METEORITES: EVIDENCE FOR ABUNDANT CRUSTAL CARBONATES?

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The 1.3 Ga old SNC (shergottites, nakhlites, and Chassigny) igneous meteorites are widely believed to come from Mars [1-3], problems with spalling large, little-shocked rocks off a Mars-sized planet notwithstanding. Although Clark [4] noted that Viking XRF analyses indicate that the martian regolith is remarkably similar to shergottites, he also noted that Ca contents are far lower in the regolith. Indeed, irrespective of the provenance of SNC's, the low Ca/Si ratios of the martian soils require an explanation. Fig. 1 shows Mg/Fe vs. Ca/Si for SNC's and for the composition that Clark [4] derived to be representative of the regolith at both landing sites, based on averaged data for deep, loose fines [7] (analyses of shallow "duricrust" samples are scarcely different). Mg/Fe is used instead of Mg/(Mg+Fe) in order to facilitate interpretations of error bars and possible mixing lines. Fig. 1 shows error bars derived, conservatively, by simply summing the errors estimated by Clark [4]. Viking data are imprecise for most elements, but among 16 analyses reported from two sites [7], Ca/Si ranged from 0.192 to 0.213. The correlation among SNC meteorites on Fig. 1 indicates that all SNC meteorites with low Mg/Fe have high Ca/Si relative to the martian regolith.

Clark's [4] main conclusion was that the Viking geochemical evidence is consistent with the hypothesis that SNC meteorites come from Mars. He addressed the Ca/Si disparity only briefly, as follows: "Calculations show mineralogic starting composition can be similar if pigeonite increases at the expense of augite (constant total pyroxene). The inferred composition is then consistent with all 10 measured elements (Mg, Al, Si, K, Ca, Ti, Fe, Sr, Y, Zr) bearing on this question. An alternative explanation for Ca-deficiency is chemical weathering to produce insoluble sulfate deposits." Clark [4] is justified in doubting that the SNC's are entirely representative. Their young ages suggest that they come from the northern hemisphere, which (including both Viking sites) is dominated by relatively young volcanic plains, whereas the heavily cratered highlands that comprise the remaining 60% of the surface are 3-4 Ga old. The upper regolith is probably well mixed on a global scale by dust storms. The highlands have obviously been exposed to weathering longer; and a key weathering mechanism on early Mars may have been hydrothermal alteration of impact melts, mainly in the heavily cratered highlands [8]. Thus, the fines analyzed by Viking may comprise more material ultimately derived from the ancient highlands than from young volcanic terrains — and the highlands may be altogether different from the young volcanic terrain that putatively supplied the SNC meteorites.

However, there remain limits to the compositions that can plausibly be invoked for the unsampled crust. Assume, for the sake of argument, that the regolith materials analyzed by Viking were derived without secondary fractionation (such as differential chemical weathering; or concentration of certain elements into sedimentary rocks) from the igneous crust. It should be possible to estimate the composition of the "missing" crust (= southern highlands?) by simple mass-balance calculations. Such calculations imply that the Ca/Si ratio for the "missing" crust must be low ( $<0.20$ ), whether "H" (the fraction of the Viking regolith assumed to come from the "missing" crust) = 1% or 99%, because even an average SNC meteorite has a higher Ca/Si ratio than the regolith. Likewise, because the Viking composition is so extremely rich in Fe relative to Si, any reasonable assumption about H leads to a "missing" crust composition that is Fe-rich, with molar  $(\text{Fe}+\text{Mg})/\text{Si} = 0.3-0.5$ .

A Ca/Si ratio of less than 0.20 does not appear realistic for any major fraction of the martian igneous crust. As illustrated by Fig. 2, not only SNC meteorites, but igneous rocks from Earth, its Moon, and the parent asteroid of the eucrite meteorites — igneous rocks from all these sources, seldom have  $\text{Ca/Si} < 0.2$ , except for granitic types with molar  $(\text{Fe}+\text{Mg})/\text{Si} < 0.3$ , or else ultramafic types with molar  $(\text{Fe}+\text{Mg})/\text{Si} > 1.2$ .

Warren, P. H.

In terms of Ca/Si, the crust of Mars is presumably at least comparable to the crusts of the Moon and the Earth. Yield of crustal Ca-feldspar from planetary differentiation is probably a function mainly of: (a) pressures that prevail in the outer few hundred km of the planet, because high pressures stabilize garnet and other phases that compete with feldspar for Ca and Al; and (b) availability of Na and K, which compete with Ca for whatever crustal Al is available. In terms of internal pressures Mars is intermediate between Earth and its Moon. SNC meteorites are also intermediate in terms of crustal Na and K [2]. Thus, barring an incredibly Ca-poor highlands, the fines analyzed by Viking cannot be derived from the igneous crust without secondary (post-igneous) Ca/Si fractionation.

Secondary Ca/Si fractionation might develop as a result of differential chemical weathering leaving rinds of Ca-rich material covering exposed igneous rocks; as a result of deposition of Ca-enriched sedimentary rocks; or both. Aside from Clark's [4] brief suggestion of "insoluble Ca-sulfate deposits," Gooding (pers. comm., 1986) has suggested that Ca/Si fractionation occurs because igneous rocks weather primarily into Ca-poor clay minerals. Weathering on Mars is of course poorly understood. Some studies [9, 10] suggest that major Ca-bearing minerals on Mars tend to weather into Ca- or Ca,Mg-carbonates, but atmospheric SO<sub>2</sub> may de-stabilize surface carbonates [11]. A problem with any differential weathering model is that physical weathering tends to convert all weathering products into fines. Consider first the Ca-rich weathering rind hypothesis. Based on landform degradation rates, the rate of aeolian erosion during recent martian history has been estimated [12] to be of the order 1-100 m Ga<sup>-1</sup>. Physical weathering by heating/cooling cycles may be particularly effective on Mars, where the soil surface temperature varies by about 90 K every 25 hours [9, 13]. Attempts to scrape material from Mars rocks showed the surfaces to be strong and scratch-resistant [14]. Barring the remote possibility that chemical weathering on Mars races ahead of physical weathering (i.e., chemical weathering has produced far more rind material than has been mobilized by physical weathering), rind models cannot plausibly account for the low Ca/Si ratios of the Viking soil analyses.

Another type of differential weathering model would be to sequester Ca-rich weathering products into different sediments from Ca-poor weathering products. Conceivably sorting by grain size and/or shape would tend to deposit the Ca-rich materials deeper than the Ca-poor materials, leading to a low Ca/Si ratio for the regolith. The question then arises, what could be the Ca-rich material? Clark and Van Hart [11] argue that sulfates in the martian crust must be mainly Mg-sulfate, not Ca-sulfate. The soils analyzed by Viking have remarkably high contents of SO<sub>3</sub>, ranging from 5.9 to 9.5 wt% [7]. If crustal Ca were largely associated with sulfate, these soils should have high, not low, Ca/Si ratios. In fact, neither the Viking analyses [7] nor analyses of soil from the analogous Dry Valleys of Antarctica [15] manifest any correlation between Ca/Si and sulfate. If, on the other hand, the Ca carrier were a clay mineral, such as prehnite, it would probably not sort apart from the Ca-poor weathering products (presumably also clay minerals).

I suggest that the Ca "missing" from the Viking soils is sequestered as Ca-carbonate. Based on the Ca/Si disparity between the average Viking regolith composition and compositions of otherwise comparable igneous rocks, particularly Shergotty, Zagami, and EETA79001-B (Figs. 1-2), the mass of Ca sequestered into CaCO<sub>3</sub> is most likely roughly 3% of the mass of material that has been eroded off of igneous rocks, i.e., 3% of the combined total mass of regolith plus sedimentary rocks (assuming that Mars contains few igneous rocks formed by "recycling" of sedimentary rocks). Addition of CO<sub>3</sub> to the Ca implies that, by this reckoning, CaCO<sub>3</sub> amounts to roughly 8% of the combined total mass of regolith plus sedimentary rocks. In addition to CaCO<sub>3</sub>, martian carbonates probably include minor MgCO<sub>3</sub> and comparatively negligible FeCO<sub>3</sub>. Note that MgCO<sub>3</sub> fractionation would enhance the effect of CaCO<sub>3</sub> fractionation in terms of Fig. 1.

Other recent suggestions that abundant carbonates exist in the martian crust have

Warren, P. H.

been motivated by considerations of the  $\text{CO}_2$  budget [5,6]. The  $\text{CO}_2$  in the atmosphere, the polar caps, and adsorbed onto surfaces of silicates in the regolith [16], combined does not seem to account for the total  $\text{CO}_2$  that has been degassed since the origin of Mars. Kahn [5] also points out that the present surface atmospheric pressure of Mars, about 7 mbar, is close to the triple point of  $\text{H}_2\text{O}$ , 6.1 mbar. Liquid water facilitates carbonate formation, and Kahn suggests that the present mass of the martian atmosphere is buffered by liquid water. Kahn suggests that  $\text{CO}_2$  occurs mainly in carbonates formed in the regolith in association with transitory pockets of liquid  $\text{H}_2\text{O}$ , melted by heat from solar insolation. However, on Mars solar insolation can only generate temperatures above 273 K in the upper few cm of the regolith (and only in low-latitude, low-elevation regions), and high sulfate contents found in the regolith by Viking may be inconsistent with near-surface  $\text{CaCO}_3$  [11].

An alternative model is that carbonates formed during an early stage of martian history by precipitating from open ponds of water. These ancient "limestones" and/or "marlstones" would be coherent, and would have formed mainly in areas of low elevation. The bulk of such formations could easily have since been buried by complementary, Ca-depleted material. Note that additional shallow carbonates might still form in association with Kahn's [5] transitory liquid water pockets. The key requirement is to segregate a considerable mass of Ca-carbonate apart from the homogeneous, wind-stirred upper regolith analyzed by the two Viking landers. Formation of the equivalent of a global shell of Ca-carbonate 20 m thick would suffice to remove 1000 mbar of  $\text{CO}_2$  from the martian atmosphere. Carbonate formation may have irreversibly depleted what was once a far more massive  $\text{CO}_2$ -dominated atmosphere. Warming by the greenhouse effect from such an atmosphere may have once allowed liquid water to exist on Mars [5,6].

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